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# **Charge-Transfer Induced Dissociation in the $\text{H}^+(\text{H}_2\text{O})_3$ –Ar collisions observed with the COINTOF mass spectrometer**

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## **ABSTRACT**

Electron-capture in collisions of singly charged protonated water cluster  $\text{H}^+(\text{H}_2\text{O})_3$ , ions with Ar atoms is studied at the impact energy of 8 keV in the frame of the COrelated Ion and Neutral fragments Time-Of-Flight, COINTOF, technique. In contrast to methods based only on the detection of the charged fragments, dissociation induced by collisional-excitation and electron-capture induced dissociation can be simultaneously recorded in the present set-up. Time of flight measurement of both neutral and corresponding charged species resulting from the charge-exchange process leads to the direct observation of the dissociation of the neutralized protonated water cluster. Thus, the present COINTOF method provides new valuable insights into the collision processes through the detection of produced neutral fragments. Moreover, it opens new possibilities to measure kinetic energy release also in the dissociation of the produced neutrals, which is our future endeavour in the development of the presented COINTOF set up.

## INTRODUCTION

The investigation of collisions between ions and neutral targets is of great importance in fundamental sciences such as astrophysics [1], atmospheric science [2], analytical chemistry [3] or plasma physics [4] but also in technology applied to medicine [5,6,7]. For instance, the atmospheric plasma sources used in medical applications are based production of the  $O^{\bullet}$ ,  $HO^{\bullet}$  and the  $H^{\bullet}$  radicals in the plasma from the gas mixture and the moisture from the ambient air [6]. These radical species are responsible of the bactericidal effects of the plasma. Another example concerns the radiation sciences field and the subsequent processes arising after the energy deposition into the irradiated medium. Indeed the first primary energetic particles produce secondary species, ions, electrons and excited molecules that further interact with their surroundings. Since water is the major constituent of biological medium can exist as clusters [8,9,10] it is these ion clusters may after their creation induce physical chemistry to the medium. Thus the knowledge of the dissociation products, i.e., the ions and more particularly the neutral fragments, from any step following the energy deposition is necessary for a deep comprehension and description of the collision processes, and for a potential improvement of an application.

The interaction of the colliding partners may lead to their fragmentation via the dissociation induced by collisional excitation and the charge transfer reactions. The fragment products, which are the signature of a collision process, are traditionally identified by mass spectrometry techniques. The ion fragments can be detected nowadays with a remarkable mass accuracy by mass spectrometry techniques [11,12]. In contrast to detection of ionic fragments, providing information on the neutral species (nature and number of the formed species, energetics, ...) which are important for the understanding of the spread of the deposited energy in an irradiated system remains a challenge. Experimentally it often requires

the ion precursors to be accelerated to high energies ( $>20\text{keV}$ ) [13,14,15]. Collecting ions in coincidence with the neutral species produced from a single collision event and their correlation is a major step towards the complete description of the collision. Such experiments are scarce since it requires a multi-detectors setup [16,17,18,19]. Recently, we have developed a new type of mass spectrometer, the Correlated Ion and Neutral Time Of Flight mass spectrometer, COINTOF\_MS, that allows the detection of ions and neutral fragments produced from a single dissociation event on the same Micro Channel Plate (MCP) detector [20,21,22]. A statistical analysis of a large number of recorded single dissociation events provides valuable information about the collision processes without losing the information on the individual fragmentation pathway [20,23].

In the present contribution, we investigate the fragmentation of 8 keV protonated water trimer,  $\text{H}^+(\text{H}_2\text{O})_3$ , in collision with argon atom target. We show the versatility of the COINTOF\_MS technique that allows to observe either the dissociation induced by collisional excitation only, or simultaneously with the dissociation induced by the charge transfer reaction. Furthermore, this method provides also information on the produced neutral species (e.g., number of neutral fragments, ...) along with the respective ion fragment within a given dissociation channel.

## EXPERIMENTAL PROCEDURE

The apparatus used for the present investigation of  $\text{H}^+(\text{H}_2\text{O})_3/\text{Ar}$  collisions has been described in detail elsewhere [20-23]. Consequently, only a brief description is given here. Protonated water clusters are produced by electron impact after the supersonic expansion of water vapor into the chamber maintained at the operating pressure of approximately  $1.0 \times 10^{-4}$  mbar. After their formation they are accelerated to 8 keV, in this work, and mass selected by a

double focusing  $E \times B$  sector field mass spectrometer [20,24]. The energy and mass-selected protonated water trimer  $H^+(H_2O)_3$  beam crosses an effusive argon gas jet for which the density is controlled in order to ensure single collision condition [23]. All produced fragments from the interaction of each single  $H^+(H_2O)_3$  precursor cluster ion with an Ar atom target are detected by the COINTOF\_MS [23] and recorded as following. The COINTOF\_MS device is subdivided into three regions: (1) the collision, (2) the acceleration and (3) the field-free region. In the collision region an electric field of 300V/cm can be applied to extract the charged species. These are further accelerated to 1.8kV in the second region before reaching the field-free region and finally impinging upon the MCP detector. It is important to note here that the extraction field in (1) is not mandatory since the acceleration region (2) suffices to separate in time the arrival of an ion and neutral fragments at the detector. The neutral fragments keep their initial velocities and reach the detector unaltered by the electric fields. The acquisition system consists of a combination of a fast Analog Digital Converter (ADC, 8GHz-10bits, Acqiris®) and a Time Digital Converter (TDC L3377 Lecroy®). An acquisition time window of typically 4 $\mu$ s ensures that all possible ion and neutral fragments produced *from one single dissociation event* are collected and recorded before another dissociation event occurs. The acquisition time window is triggered by the arrival of the first fragment on the detector. The arrival time of the neutral fragments is used as the time reference within a given dissociation event. Thus the time difference between the arrival time of the ion and the neutral products,  $\Delta T$ , is characteristic to the mass of the charged species and produces characteristic COINTOF spectrum shown in Figure 1. It is also possible to program the ADC instrument for the recording of a specific dissociation channel (i.e., at a given  $\Delta T$ ) while the TDC device records all possible channels.

## RESULTS and DISCUSSION

In the collisions of 8 keV  $\text{H}^+(\text{H}_2\text{O})_3$  water clusters with Ar atoms many processes may occur. In this velocity range the inelastic scattering leads to the fragmentation of the precursor ion into a charged and one or many neutral products. The Figure 1a represents a typical COINTOF mass spectrum without applying an extraction field. By comparing the measured  $\Delta T$  with the ion trajectory simulation using SIMION software, they are characteristic of the production of (A)  $\text{H}^+(\text{H}_2\text{O})_2$ , (B)  $\text{H}^+(\text{H}_2\text{O})$ , and (C)  $\text{H}^+$  ion fragments. Fig.1a,b are constructed from a large number of single dissociation events (216000 and 60000 single dissociation events, respectively). Figure 2 displays three examples of individual fragmentation events recorded by the ADC instrument. They are associated to the dissociation channels producing the (A)  $\text{H}^+(\text{H}_2\text{O})_2$ , (B)  $\text{H}^+(\text{H}_2\text{O})$  and (C)  $\text{H}^+$  ion. Fig 2a shows two peaks, the first being attributed to the  $\text{H}^+(\text{H}_2\text{O})_2$  ion while the second to the neutral  $\text{H}_2\text{O}$  fragment according to the value of  $\Delta T$ . In the Fig 2b two neutral fragments attributed to two water units are observed with the  $\text{H}^+(\text{H}_2\text{O})$  ion fragment. Finally in Fig.2c, the production of the  $\text{H}^+$  fragment ion (first peak) is accompanied by three further fragments at most, suggesting three water units. In a collision process, some of the kinetic energy is transferred into the internal energy of the colliding partners. The local electronic excitation will influence the subsequent fragmentation. For various molecular ion/Ar target collision experiments in the keV energy range, it was shown that in most cases ( $\sim 80\%$ ) the internal energy gained in the collision was below 8.5 eV, whereas the internal energy of more than 12 eV was present only in  $\sim 2\%$  [25,26,27,28]. Because it has been shown that fragmenting a water unit within a water cluster requires excitation energies above 12 eV [29], it is very likely that in the present experiment the loss of water unit(s) from the precursor ion is the most dominant dissociation process. The production of  $\text{H}^+$  ions is reported in contrast to earlier CID experiments undertaken at energies up to 100 eV [30] or at 50 keV [31]. Indeed, the proton affinity of water trimer is

estimated to be 9.21 eV [32]. According to the distribution of the energy transferred in the collision, the production of proton is energetically unfavourable under the present experimental conditions, however, it remains accessible in agreement with the reported mass spectrum in Fig1.

In Figure 1b, an additional feature appears in the mass spectrum at  $\Delta T = 1725.3 \mu s$ , when an extraction field is applied. From the simulation of the ions trajectory, this  $\Delta T$  value corresponds to the  $Ar^+$  ion that is formed through charge transfer reaction. Indeed starting from thermal velocities of the neutral Ar target, the nascent  $Ar^+$  ion formed via the charge exchange reaction acquires the kinetic energy given only by the extraction and the acceleration fields that is a total of 2kV. Bearing in mind that the formed neutral species keep the velocity of the 8keV parent ion (in addition to the kinetic energy release by the fragmentation), they are expected to reach the detector well before the  $Ar^+$  ion. Figure 3 exhibits two examples of a single dissociation event recorded by the ADC device. In contrast to Fig.2, multi-peaks are observed at short arrival times and only one peak at a longer arrival time. The charge exchange process would leave  $[H(H_2O)_3]^{**}$  in some electronically excited state which would undergo dissociation into  $H^\bullet$  radical and  $3H_2O$  corresponding to the four peaks observed at early arrival times in Fig. 3b. Due to the high reactivity of the  $H^\bullet$  radical, it might react with  $H_2O$  within the neutralized precursor leading to the production of  $H_2 + \bullet OH + 2H_2O$ . In contrast, Fig.3a shows the presence of only two peaks associated to the neutral fragments. It is not clear yet whether this is due to the efficiency of the detection of neutral fragments or due to the dissociation process producing for instance  $H^\bullet$  and  $(H_2O)_3$  [33].

## CONCLUSION

The present contribution, we showed that the COINTOF mass spectrometer is capable to provide information on both collisional dissociation and charge transfer dissociation reactions. By a simple change in the extraction voltage, it is possible to study only the collisional-excitation induced dissociation process. For any of the two mechanisms mentioned above in these collision experiments undertaken at low energy (i.e., < 10 keV), the recorded ADC signal for a single dissociation event provides information on the number of neutral fragments produced along with its ion counterpart. The results showed that the charge-exchange process leads to the neutralization of the  $\text{H}^+(\text{H}_2\text{O})_3$  ions followed by a fragmentation into at most 4 neutral species. Further analysis of the time and position distributions of the neutral fragments will provide information on the energetics of the reaction (kinetic energy releases, ..). Although the  $\text{H}^+(\text{H}_2\text{O})_3\text{-Ar}$  reaction is not directly biologically relevant, nevertheless our results demonstrate the ability of the COINTOF technique to provide new insights for the description of radiation action at the nano-scale level.

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## FIGURE CAPTION

**FIGURE 1:** The COINTOF mass spectra: (a) without applying the extraction field in the collision zone and (b) when applying 300V/cm. The fragmentation of the  $\text{H}^+(\text{H}_2\text{O})_3$  precursor ion produces (A),  $\text{H}^+(\text{H}_2\text{O})_2$  (B)  $\text{H}^+(\text{H}_2\text{O})$ , and (C)  $\text{H}^+$  from collisional excitation and (D)  $\text{Ar}^+$  from charge transfer.  $\Delta T_A$ ,  $\Delta T_B$ ,  $\Delta T_C$  and  $\Delta T_D$  represent the difference between the arrival time of the neutral and the ion fragment that is characteristic of the mass of the charge species (see text).

**FIGURE 2:** Collisional-excitation induced dissociation process: examples of a single dissociation event recorded by the ADC electronics for different fragmentation channel characterized by  $\Delta T$ : (a),  $\text{H}^+(\text{H}_2\text{O})_2$  (b)  $\text{H}^+(\text{H}_2\text{O})$  and (c)  $\text{H}^+$ .

**FIGURE 3:** Examples of single dissociation events recorded by the ADC electronics for the charge transfer process. The peaks observed at the earlier arrival times correspond to the neutral fragments (see text). The spread in their arrival times reflects the kinetic energy release resulting from the electron-capture induced dissociation.

**FIGURE 1**

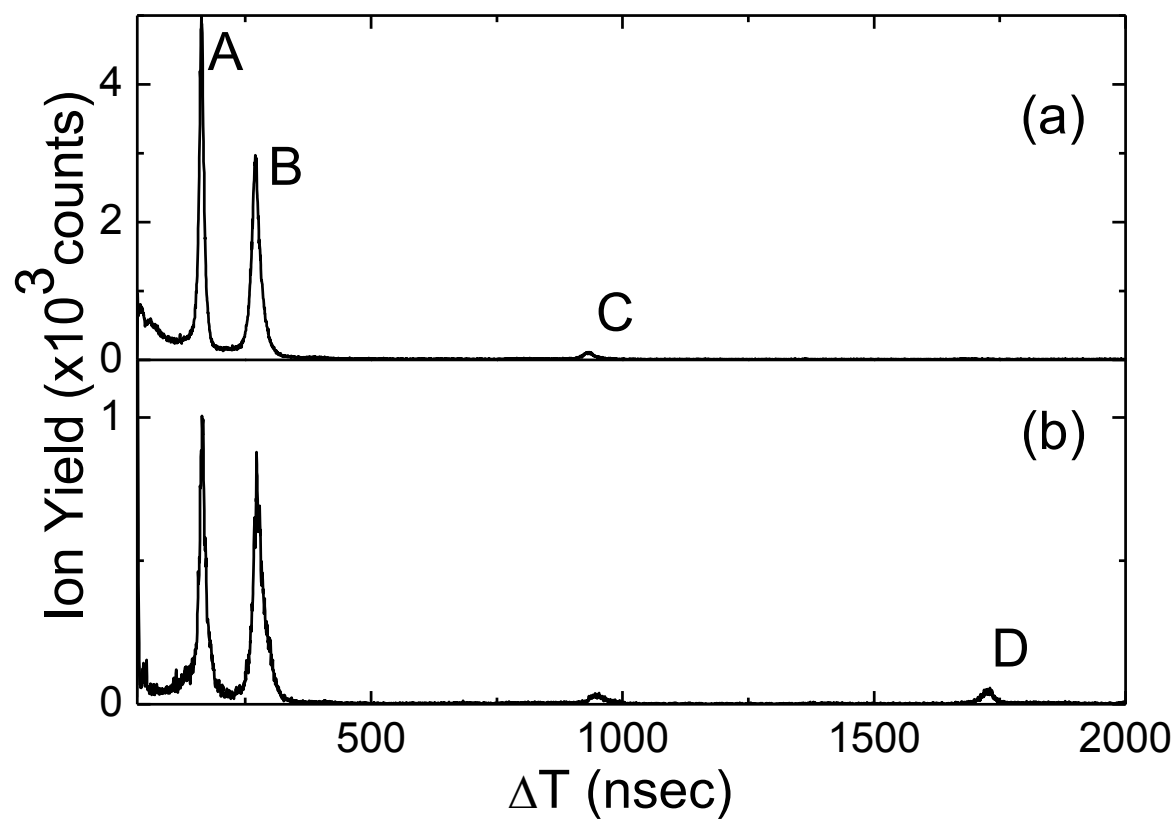
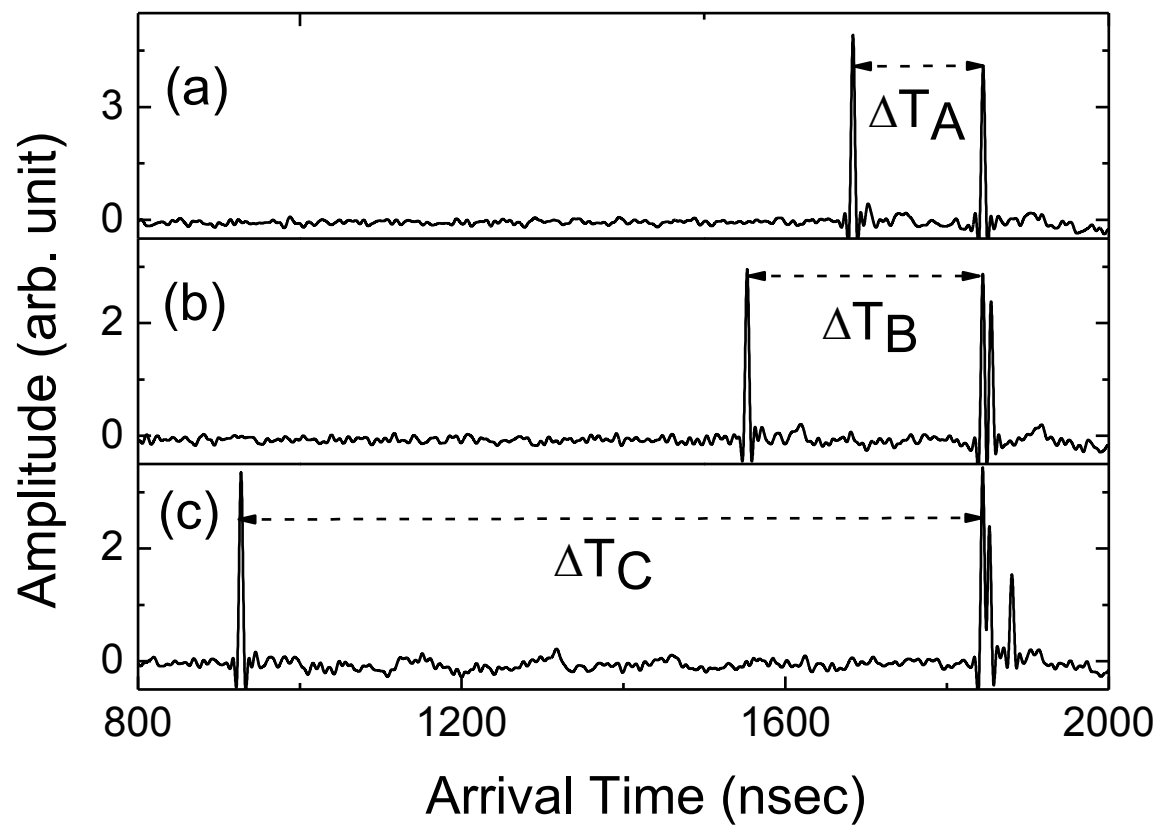
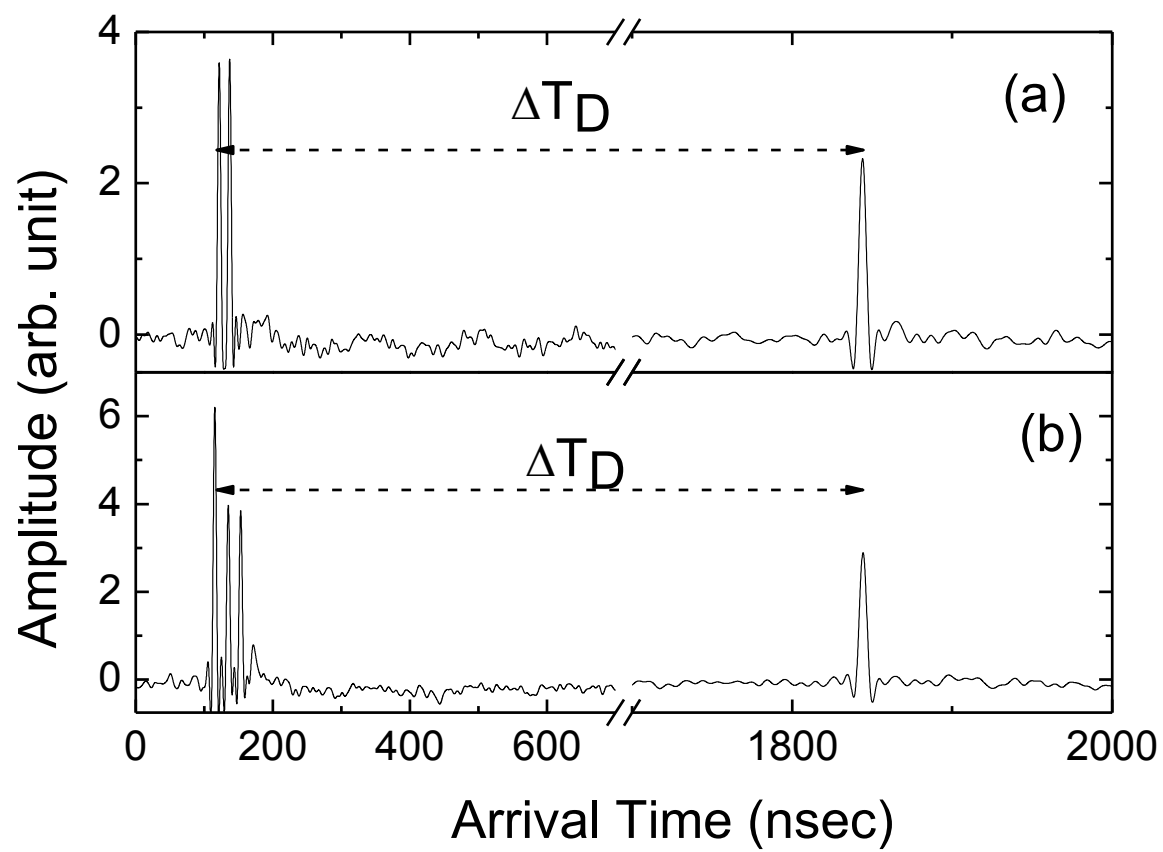


FIGURE 2



**FIGURE 3**



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